PETROGRAPHIC CHARACTERIZATION OF LUNAR SOILS: APPLICATION OF X-RAY DIGITAL-IMAGING TO QUANTITATIVE AND AUTOMATED ANALYSIS.

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The rocks and soils of the Moon will be the raw materials for various engineering needs at a lunar base, such as sources of hydrogen, oxygen, metals, etc. The material of choice for most of the bulk needs is the regolith and its < 1 cm fraction, the soil. For specific mineral resources it may be necessary to concentrate minerals from either rocks or soils. Therefore, quantitative characterizations of these rocks and soils are necessary in order to better define their mineral resource potential. However, using standard point-counting microscopic procedures, it is difficult to quantitatively determine mineral abundances and virtually impossible to obtain data on mineral distributions within grains. As a start to fulfilling these needs, Taylor et al. [1] and Chambers et al. [2] have developed a procedure for characterization of crushed lunar rocks using x-ray digital-imaging. In this paper, we describe the development of a similar digital-imaging procedure for lunar soils as obtained from an Oxford Instruments, Inc. Energy-Dispersive-Spectrometer unit (EDS) attached to a Cameca SX-50 EMP.

SOIL FORMATION AND CONSTITUENTS: Lunar soil was formed by three processes: 1) **comminution** - the disaggregation of rocks and minerals into smaller particles by micrometeorites; 2) **agglutination** - the welding of mineral and rock fragments together as a result of melts derived from micrometeorite impacts; 3) **spallation and implantation** - the addition of important elements derived from solar winds (including H_2, ^4He, ^3He, and CO) to the soil [3, 4].

These soils contain monomineralic (clean) particles and fragments of basaltic and highland rocks (multimineralic), melt rocks, microbreccias, impact glasses, pyroclastic glasses (beads), and agglutinates. Of these different soil grains, the unique constituents are the **agglutinates**. Agglutinates contain a myriad of single-domain (40-300 Å in size) and larger native iron (Fe^0) spheres formed as a product of the extreme reducing environment imposed on the silicate melt by the presence of solar-wind implanted H_2 and C [5]. In addition, release of the solar-wind implanted volatiles during this melting process creates abundant vesicles. The abundance of tiny Fe^0 spheres and the presence of vesicles serve as a means of petrographically distinguishing
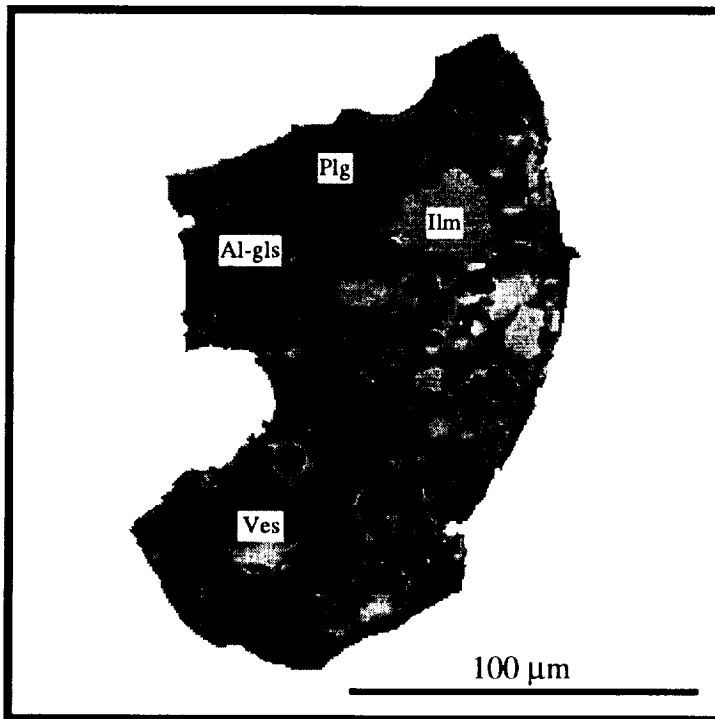

Figure 1. Digital image of a typical agglutinate from lunar soil 10084, 74-150 μm size fraction.

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agglutinates from other impact products [6].

DIGITAL IMAGING OF LUNAR SOILS: In order to determine the phases and grains present in lunar soils by x-ray mapping, qualifying chemical and petrographic data were established through an iterative process involving traditional microscope techniques and EMP image analysis. The *Featurescan* software utilizes user-defined chemical and physical criteria to identify phases (e.g., hi-Ca and hi-Al are indicative of plagioclase), and because of the differences in rock and soil types amoung the two regions of the Moon (i.e., the highland and mare), the same criteria can not be used all over. In this study, user-defined criteria are established for a mare basalt soil, 10084, because such soils have greater potential for resource utilization [4].

APPLICATION: The "imaging soil petrography" technique of this study was developed using various size fractions and magnetic splits of a hi-Ti, mature mare soil, 10084. This soil was chosen because of its petrologic complexity and vast array of petrographic constituents (i.e., from agglutinates to clean mineral fragments to pyroclastic glass beads). A secondary backscatter electron (BSE) digital image of a typical agglutinate from 10084 (74-150 μm size fraction) is shown in figure 1. Note the distinct holes (vesicles) and high glass content, both criteria used for classification. Table 1 compares data for the 44-74 μm fraction of 10084 acquired from this study with petrographic particle-count data obtained by Taylor and Oder [4]. The minor differences in the data are attributed to the subjectiveness of the defining criteria. The table is broken into four groups: (I) particles containing glass, (II) monomineralic fragments, (III) basalts, and (IV) iron sulfides.

Group I soil grains, with the exception of agglutinates, are defined entirely on glass content. Morphology is used as an additional criteria for defining

Table 1. Digital-imaging obtained particle percentage data for lunar soil 10084, 44-74 μm, as compared with microscopic data of Taylor and Oder [4].

	particle	this study	Taylor and Oder
	agglutinate	45.31	47.1
	microbreccia	6.75	0.9
(I)	melt rocks	17.38	14.9
	impact glass	6.62	5.9
	beads	0.52	3.8
	ilmenite	5.84	7.0
(II)	plagioclase	2.89	6.6
	pyroxene/olivine	1.12	1.6
(III)	basalt	13.38	11.6
(IV)	Fe/FeS	0.20	0.2

agglutinates. Therefore, fragments classified as agglutinates contain > 15% glass and have vesicles. Microbreccias, melt rocks, impact glasses, and beads contain 10-30%, 30-80%, 80-100%, and 80-100% glass, respectively. Beads are distinguished from impact glasses on the basis of texture (i.e., they are round). Except for ilmenite grains, particles containing 80-100% of one mineral (e.g. pyroxene, plagioclase) are placed in Group II. In this classification, fragments containing 40% ilmenite are considered (as per Taylor and Oder [4]) monomineralic. Group III (basalts) consists of soil grains that contain two or more major phases (e.g., pyroxene and plagioclase). Particles classified in Group IV (Fe/FeS) are defined according to chemistry (i.e., fragments containing low Ti and Al, and high Fe and S).

CONCLUSIONS: Essentially, the procedures outlined in this paper using digital-imaging analysis should be useful in quantitatively characterizing lunar soils for scientific purposes as well as for evaluations of potential resource utilization.

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TEKTITES FOUND IN THE RUINS OF THE MAYA CITY OF TIKAL, GUATEMALA;

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Tektites are natural glasses quenched from superheated melts produced, and ejected at relatively large velocities, by impacts on the surface of the Earth. Some of their most obvious petrologic characteristics (e.g. reduction, volatile depletion, and lack of crystallites) are a consequence of this superheating. To date, tektites have been reported from 5 strewnfields, in some cases associated with known source craters, but tektites are probably produced in all sufficiently large terrestrial impacts. Unusual glass nodules discovered by archeological studies in the Maya city of Tikal, Guatemala show petrologic signatures characteristic of tektites and may represent products of an as yet unknown impact.

Provenance: During sorting and classification of glass artifacts found in excavation of the Maya ruins at Tikal, Guatemala, 11 unworked glass nodules were separated on the basis of their shape, size (See Figure 1) and colour (clear brownish green) from the commonly found obsidian artifacts (1). The nodules were found in general excavations widely scattered through the city, mostly in small structure groups that are presumed to have been residences. We assume that the nodules were collected at points unknown and transported by the Maya to the city of Tikal; no other similar nodules have yet been reported from other Maya archeological sites.

Petrography: The 3 nodules studied to date are composed of clear glass lacking any phenocrysts, microlites or schlieren visible to optical or SE microscopes. On this basis a possible impact origin had been previously suggested (2). Spherical vesicles ranging up to ~0.5 mm occur similar in abundance and size to those found in philippinites. Although the nodules' surfaces are pitted from presumed dissolution, no surficial alteration rims were obvious in cross section.

Composition: The tektites' composition has been studied by electron microprobe, INAA, ICP-MS and XRF. All 3 samples yield similar compositions of major, minor and trace elements and results are consistent with previous work (2). The silica abundance is ~62%, a value lower than those exhibited by most tektites excepting those of Cretaceous/Tertiary (K/T) age. Indeed, the major and minor element abundances are similar to those of the K/T tektites causing us to speculate that the Tikal tektites might have been transported from K/T boundary sections that outcrop near Tikal. However, trace elements, such as the REE, revealed patterns distinct from those displayed by the K/T tektites (3,4). In general, all lithophile incompatible elements are depleted relative to abundances found in the other four tektite groups consistent with the depletion in Si although an upper crustal affinity is evidenced.

Water Content: Tektites are depleted in all volatiles relative to other natural glasses; water contents are of the order of 100 ppm which is more than an order of magnitude less than found in the driest volcanic glasses (5). The water content of the 3 samples was studied using IR spectrometry yielding water contents of 60 to 80 ppm, values typical of tektites.

Fe^{+3}/Fe^{+2} ratio: Because of superheating, tektites display reduced chemistry such as Fe^{+3}/Fe^{+2} ratios approaching zero in contrast to terrestrial volcanic glasses that exhibit ratios of near unity or above. Mossbauer studies of one of the samples detected no Fe^{+3} consistent with extreme reduction. Magnetic studies of all 3 samples reveal magnetic susceptibilities, magnetizations and Curie constants generally consistent with reduction levels as found in other tektites (6). The temperature-independent susceptibility is higher than that of most tektites, but is similar to those of Haitian K/T tektites. The Curie constants are also similar to those of the Haitian glasses.

Age: The age of the tektites was expected to be 10 to 100 million years so an Ar-Ar study was planned with an irradiation optimized for an age of this order. However, a much younger age of

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800,000 ± 100,000 years (2σ) was found based on an isochron defined by the 3 samples. This experiment will be repeated with an irradiation optimized for this younger age and larger samples to provide more radiogenic ^{40}Ar.

Conclusions: The Tikal nodules are of impact origin based on their petrologic character and represent fusion of an upper crustal target of intermediate composition. No natural occurrences of tektites are known in the region excepting the potential occurrence of tektites produced by the Chicxulub impact of K/T boundary age or from the North American tektite strewn field of Late Eocene age. Both of these tektite producing events are excluded as possible sources for the Tikal tektites because of their greater ages. The remaining possibilities are that these tektites represent transported individuals (of unusual composition) from 1 of the 2 youngest tektite strewnfields (Ivory Coast or Australasian) or are products from an as yet unknown impact in the region. The former is regarded as unlikely based on available compositional constraints but the preliminary age datum does overlap the age of the Australasian strewn field which also exhibits considerable compositional variation (7). Additional studies will discriminate between these possibilities.

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Figure 1:   Six of the irregular nodules recovered from archeological excavations at Tikal, Guatemala. The nodules range from 1.3 to 3.0 cm in greatest dimension. The nodules' shapes are apparently the result of pitting and spalling from originally comparatively equant to teardrop shapes (Courtesy of Tikal Project, University Museum).

HIGH PRESSURE AND TEMPERATURE METAL-SILICATE PARTITIONING BEHAVIOR OF MODERATELY SIDEROPHILE ELEMENTS: IMPLICATIONS FOR THE EARLY HISTORY OF THE EARTH

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Introduction. It has been known for some time that siderophile element abundances in the Earth's mantle are too high for metal to have been in equilibrium with silicate [e.g., 1], particularly if equilibrium was established at low pressures and temperatures near the surface of the accreting Earth. Although many hypotheses have been proposed to account for this apparent disequilibrium, none has been entirely satisfactory [2]. Murthy [3] proposed that the problem may be reconciled if metal-silicate equilibrium was established at high pressures and temperatures. We have performed experiments on the distribution of siderophile elements between liquid metal and liquid silicate at 100 kbars and 2000 °C. These experiments demonstrate that it is unlikely that siderophile element abundances were established by simple metal-silicate equilibrium at any combination of temperature and pressure, and that core formation in the Earth was probably a mixture of complex physical and chemical processes.

Experimental Techniques. Experiments were conducted in the 1200 ton multianvil apparatus at the Bayerisches Geoinstitut. The sample was contained in either MgO or Al_2O_3 capsules which were surrounded by a MgO sleeve contained within a cylindrical $LaCrO_3$ heater with a geometry designed to minimize thermal gradients across the sample [4]. The sample assembly consisted of a MgO (+5 wt.% Cr_2O_3) octahedron with an edge length of 18 mm. Temperature was monitored with a 0.25 mm diameter W3%Re/W25%Re thermocouple in contact with the sample capsule.

The starting material consisted of a synthetic basalt prepared by mixing together reagent grade oxides in the following proportions: 50 wt. % SiO_2, 19 wt. % FeO, 13 wt. % Al_2O_3, 11 wt. % CaO, and 7 wt. % MgO. This synthetic basalt was doped with 1.5 wt. % each of NiO and CoO, or MoO_2 and WO_2, or V_2O_3, Cr_2O_3, and MnO. These mixtures were melted and quenched to a glass and then ground back to a powder. This glass powder and Fe metal filings were mixed together in an approximately 50-50 ratio by mass.

The samples were first brought to a pressure of 100 kbars, and then were heated to 1600 °C and held at that temperature for 45-60 minutes to sinter the capsule material in order to minimize its subsequent chemical interaction with the sample. The temperature was then raised to 2000 °C and held there for 3 minutes. At this temperature and pressure, both metal and silicate are liquids. The charges were quenched rapidly (to less than 300 °C in 1 second) by turning off the power to the $LaCrO_3$ furnace.

Experimental results. The samples were analyzed with a Cameca SX50 electron microprobe. The initially homogeneously distributed metal filings had largely segregated into a single spheroid in the center of the charge. The silicate liquid did not quench to a glass but segregated into two phases with a dendritic texture. Thus to determine the composition of the silicate liquid prior to quenching the electron beam was rastered over an area approximately 20 μm on a side, and 30 to 40 analyses were taken and averaged together. For the metal a point beam was used. For major elements a beam current of 30 nanoamps and a counting time of 15 seconds were used. For the trace elements beam currents between 125 and 250 nanoamps and counting times of up to 10 minutes were used.

The metal-silicate partition coefficients we determined for Ni, Co, Mo, W, Fe, V, Cr, and Mn are shown in Table 1 along with their one sigma uncertainties and an estimated oxygen fugacity relative to the iron-wüstite buffer. Molybdenum and W were both below analytic detection in the silicate glass, thus lower limits for their metal/silicate partition coefficients are reported. Our results for Ni and Fe agree well with those of Walker *et al.* [5].

Discussion. In Figure 1, we compare our partition coefficients that were approximately 1.6 log units below the iron-wüstite buffer to 1260 °C, 1 bar data that were in a similar redox state. This Figure shows that the Ni and Co metal-silicate partition coefficients decrease with

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increasing temperature and pressure. Although the W partition coefficient measured in this study is only a lower limit, it is larger than its lower temperature and pressure counterpart indicating that W becomes more siderophile with increasing temperature and pressure. This result is contrary to the prediction of [3]. The Mo partition coefficient is also a lower limit. It is presently unclear whether Mo becomes less siderophile or more siderophile with increasing temperature and pressure. Because of the large variability of the lower temperature and pressure V, Cr, and Mn data, it is difficult to say what trends are present.

Although we are working under the assumption that temperature has a stronger influence on partitioning behavior than pressure, with this limited data set, we can not say for certain which variable is more important. There is evidence that pressure may play a significant role in the partitioning of siderophile elements [6].

The partition coefficients reported above may be used to evaluate whether simple high temperature equilibrium between metal and silicate during accretion of and core formation in the Earth can account for the abundances of Ni, Co, W, Mo, V, Cr, and Mn in the upper mantle of the Earth. In particular, the approximately equal abundances of Ni, Co, and W constitute a powerful test. Simple mass balance between the core and the mantle of the Earth may be used to calculate what metal-silicate partition coefficients are necessary to produce the observed abundances of these elements in the mantle. Calculated metal-silicate partition coefficients are given in Table 1. To first order, mean core-mantle partition coefficients for Ni, Co, and W need to be 40 ± 5. Inspection of Figure 1 indicates that this condition is not satisfied in the pressure range of 1 bar to 100 kbars and temperature range of 1260 °C to 2000 °C. Extrapolation of these results to higher temperatures and pressures is very uncertain, but there is little evidence that the metal-silicate partition coefficients for Ni, Co and W will ever converge on a value of 40 ± 5 for Ni, Co, and W, especially if the trends observed in Figure 1 continue.

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Figure 1: Comparison of 1260 °C, 1 bar parition coeffcients to the ones measured in this study. One bar data from [7] and [8].
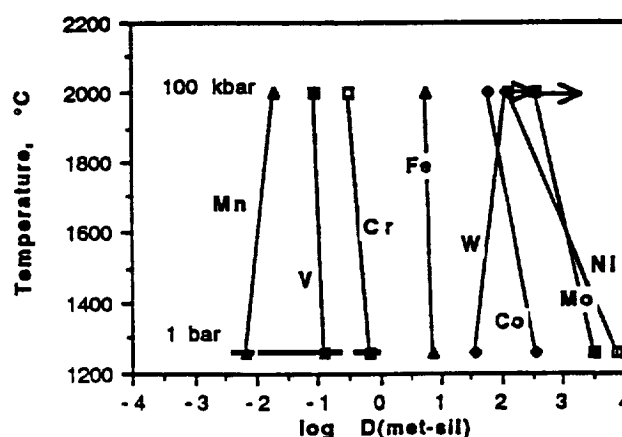
Expt.	capsule material	ΔIW	Fe	Ni	Co	W	Mo	V	Cr	Mn
888	Al₂O₃	-1.6	6.2±0.2	135±15	60±3	*	*	*	*	*
891	MgO	-2.3	12.4±0.4	247±44	106±16	*	*	*	*	*
895	Al₂O₃	-1.6	6.0±0.1	*	*	>123	>360	*	*	*
912	Al₂O₃	-1.6	6.5±0.5	*	*	*	*	0.09±0.01	0.32±0.03	0.016±0.002
D(met/sil) required for core/mantle equilibrium			16	45	40	35	160	4	5	13

* = not present in charge